

Final Report for #FA2386-12-1-4092 "Carbon-coated current collectors for high-power Li-ion secondary batteries III"

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Abstract: The ultimate goal of this project is to develop a viable C-coating process of the current collector in order to improve the overall power performance of the electrode of Li-ion batteries. During this third-year period, the performance of different thickness of carbon coating on Al foil is compared. The result shows that only the samples with sufficient thickness to form conductive channel on the surface would give a positive effect on the performance. Scale up of this coating process is further developed to make 1.5 m long C-coated tape by a contentious process followed with a special batch thermal process called roll-calcination. The same positive effects seen on small samples have been reproduced.

Introduction:

The basic principle for achieving high-power capability of a battery is minimizing the overall resistance of the electrochemical system. For Li-ion batteries, much research effort has been devoted in the past to minimize the ionic diffusion resistances and electronic resistance associated with the electrode active materials. In the typical electrode configuration, the layer containing the active material is supported on a metallic current collector. The interface between the current collector and active layer imposes additional resistance to charge transfer within the electrode. This resistance source has not received sufficient attention in the past, presumably because it was not considered of significance for the low-power Li-ion electrode materials. However, the advancement in the material synthesis technologies has reduced the ionic and electronic resistances associated with the active materials to certain point that they become competitive to the other resistance sources. Thus, the significance of the electronic resistance at the active layer/current collector (AL/CC) interface is worthy of careful re-examination.

The objects of this study is to prepare C-coated Al current collectors by two different coating processes, including high-temperature thermal chemical vapor deposition (HT-CVD) and low-temperature chemical vapor deposition (PA-CVD), and to characterize their electrochemical properties pertain to the power performance and cycling stability of Li-ion batteries. At least two beneficial effects are anticipated to result from the C-coating. For one, the C-coating removes the native surface oxide layer on the metal current collectors. For the other, the C-layer is hydrophobic in nature and hence helps to improve the interfacial bonding. Both effects are expected to reduce the AL/CC interfacial resistance. The ultimate goal is to develop a viable C-coating process of the current collector in order to improve the overall power performance and/or cycle life of the electrode of Li-ion batteries. In last year, we have developed a PA-CVD process for C deposition. The study in this year is to illustrate the effect of film thickness and to scale-up the process to manufacture a tape longer than 1 m.

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Experiment:

Surface and electrochemical analyses

The surface composition at different depth was analyzed by X-ray photoelectron spectroscopy (XPS), which employed an Al K α X-ray source operated at 15 kV and 100 W, and used a beam size of 400 μm and a pass energy of 20 eV for spectrum acquisition. Sputtering gun was operated at 3 kV and 1 μA with a sputtering area of 2 mm x 2 mm. The surface hydrophobic property was determined by contact angle test (FTA105) with DI water. Raman spectrum was used to analyze the structure of carbon layer, and the wave length of laser light source is 532nm. Conductive atomic force microscope (CAFM) was used to measure the surface morphology and conductivity distribution on the Al surface.

Electron-performance for use modified Al foil as current collector of the cathode. LiFePO₄ (LFPO) was used as active materials for test, and this cathode material was purchased from Aleees company. The LFPO active layer contains 85 wt.% LFPO powder, along with 7wt% carbon conducting additives and 8wt% polymeric binder (Polyvinylidene difluoride; Aldrich). The electrodes were roll-pressed and finally dried at 150 °C for 6 hr in vacuum. The resulting LFPO electrodes have a weight of ca. 2.50 mg/cm². The electrodes were assembled with Li-foil counter electrodes to make CR2032 coin cells, and the electrolyte was 1 M LiPF₆ in a 1:2 v/v mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC; Mitsubishi Chemical). All the cells were assembled in a dry room where the dew point was maintained at between -40 and -45 °C.

Electrochemical characterizations include constant current charge/discharge (C/D) test and electrochemical impedance spectroscopy (EIS). The C/D tests were carried out with selected current rates on a battery tester (Arbin, model: MCN6410). The charge and discharge phases of a cycle were always conducted at the same selected current rate. EIS analysis (AUTOLAB, Eco Chemie PGSTAT30) was conducted with the frequency ranging from 10 mHz to 60 kHz and a voltage amplitude of 10 mV at the open-circuit voltage (OCV) of a cell.

Results and Discussion:

Optimization of carbon Thickness

The thickness of carbon coating on Al surface is adjustable by changing the flow rate of CH₄ in the plasma process. The operation parameters of plasma process are shown at Table 1. The sample with low, medium and high flow rates are respectively marked as PA-Al, PB-Al and PC-Al. All of these samples were subjected to the same thermal treatment at 550°C N₂ and named as PAT-Al, PBT-Al and PCT-Al. The photos of the sample before and after the thermal process are shown as Fig. 1. It is clear that the tape becomes more brownish when CH₄ flow rate is getting higher, while the color becomes lighter after the thermal treatment.

Raman spectra are shown in Fig. 2. The peaks corresponded to the sum of G band (around 1590 cm⁻¹) and D band (around 1350cm⁻¹) of C, and the intensities of the peaks increase, indicating increasing amount of C deposition, with increasing CH₄ flow rate. The profile of each spectrum can be de-convoluted with two Gassian peaks to get more detail information (Table 2.). The width of the G band decreases after thermal treatment. Sharper G band indicates increased crystalline of this carbon structure, which might give better electrical conductivity as compared with the amorphous carbon.

Table 1. parameters for two step of plasma process.

<i>step</i>	<i>1st</i>	<i>2nd-sample A</i>	<i>2nd-sample B</i>	<i>2nd-sample C</i>
CH ₄ flow rate (sccm)	3.5	10	12	14
N ₂ flow rate (sccm)	0.2	0.2	0.2	0.2
Pressure (mtorr)	2	6.1	7	8.3
Voltage (V)	1500	1050	900	900



Figure 1. the photo of PA-Al foil(a), PB-Al(b), PC-Al(c), PAT-Al foil(d), PBT-Al(e), PCT-Al(f).

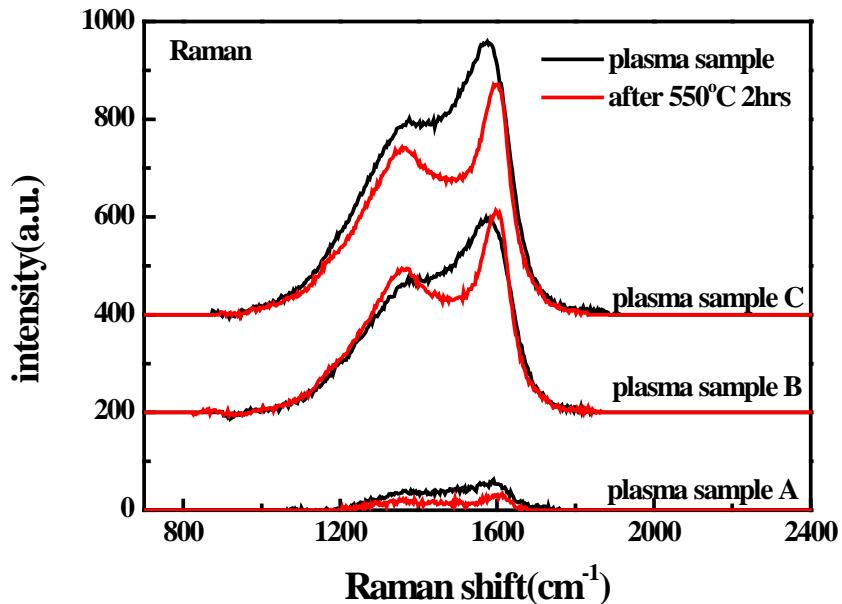


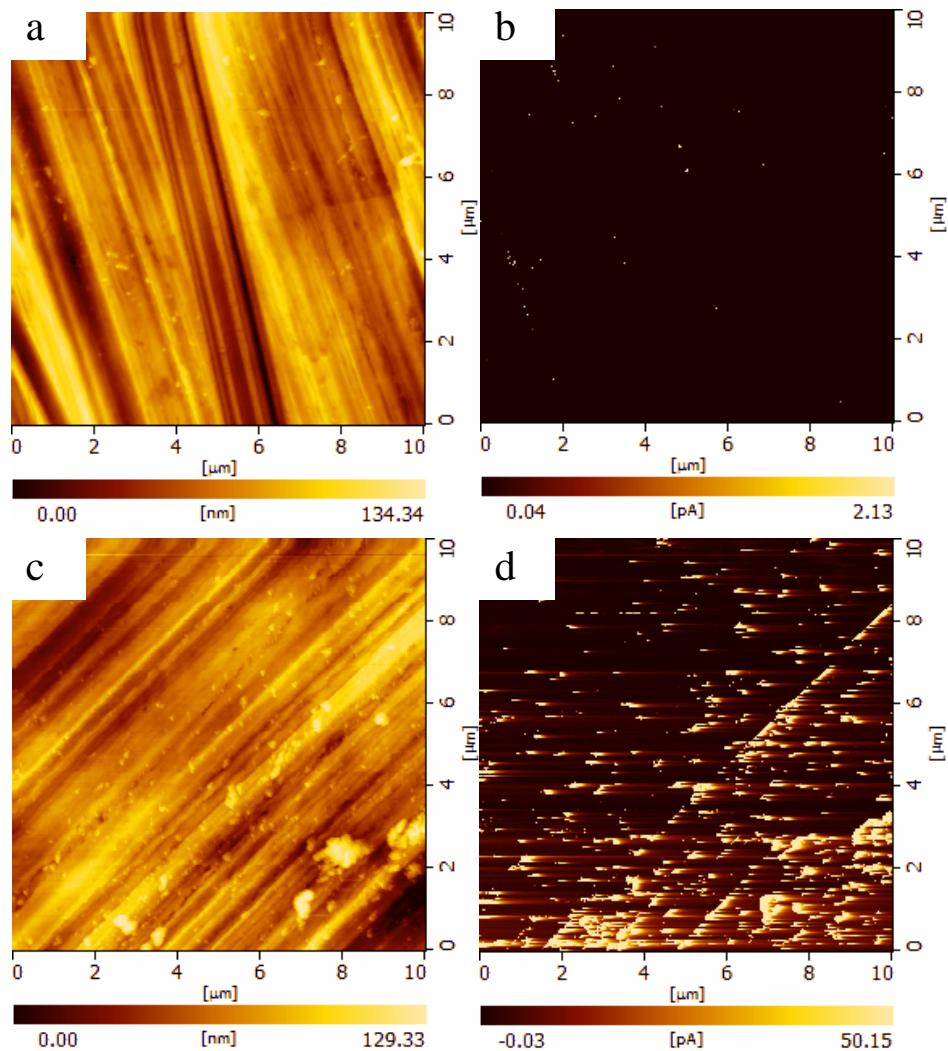
Figure 2. Raman spectrum of plasma carbon coated Al foil PA-Al, PB-Al, PC-Al and the foils after clip-calcination.

Table 2. Fitted parameters form Raman spectrum.

<i>Raman</i>	<i>Center</i>	<i>Area</i>	<i>Width(FWHM)</i>	<i>Height</i>
PA-Al	G 1582.1	6723.6	112.1	47.9
	D 1398.9	9456.1	195.2	38.6
PB-Al	G 1582.7	35226.9	106.2	264.7
	D 1407.5	99105.8	285.1	277.3
PC-Al	G 1579.1	47341.2	103.3	365.7
	D 1397.6	149179.7	298.1	399.3
PAT-Al	G 1600.2	2121.7	62.6	27.1
	D 1404.4	4845.6	212.6	18.2

PBT-AI	G	1597.1	28666.7	74.9	305.5
	D	1390.9	98860.5	283.6	278.2
PCT-AI	G	1597.0	31750.6	74.9	338.3
	D	1391.8	121294.2	297.1	325.7

Conductive atomic force microscope (CAFM) is used to acquire the information about the conductivity distribution on the surface. Keeping the potential of the conductive tip at 3V, the images of height and images of current passing through the tip are shown in Fig. 3 (a-f). From the image of the current distribution, the one with thinner layer of carbon coating (PAT-AI) gets very tiny amount of current as similar as the one without any treatment, and it might be due to insulation of the surface oxide layer formed in the thermal process. On the other hand, the surfaces of the medium (PBT-AI) and thick (PCT-AI) carbon layers show some high current areas. This means carbon layer should be thick enough for getting the high conductive passage on the surface.



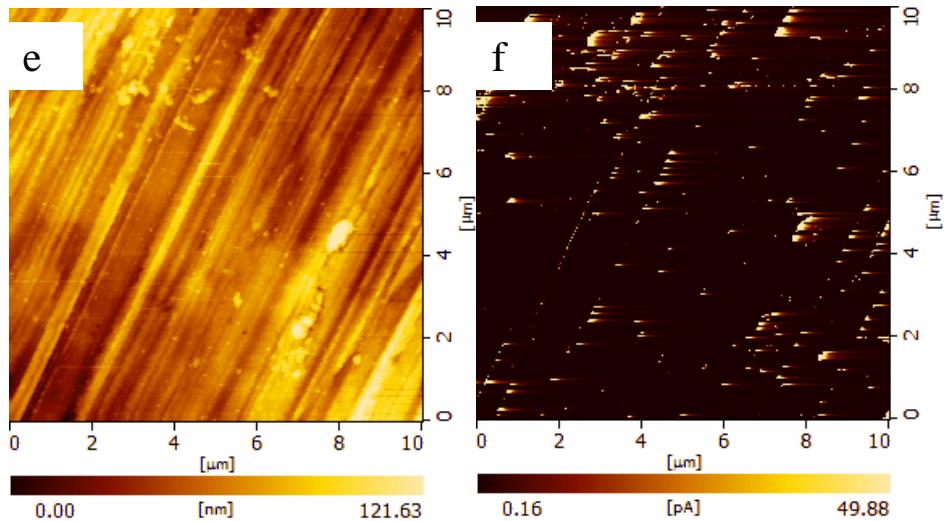


Figure 3 (a-f). Height image and current image of PAT-Al (a,b), PBT-Al (c,d) and PCT-Al (e,f) with 3V on the scanning tip.

The performance of the LFPO electrodes using these current collectors with different thickness of carbon layer has been compared. The rate capacities of the electrodes with three kinds of current collectors were shown in Fig. 4. It shows the rate capacity of LiFePO₄ (LFPO) get poorer when using PAT-Al as current collector, and this might be attributed to isolation of oxidation layer formation after thermal process. However, the rate capacity increases when PBT-Al and PCT-Al are used as current collector, and the enhancement for capacity is much enhanced particularly at high C-rate (10 C). The resistance effect from different current collectors can also be observed from the charge/discharge voltage curves (Fig. 5). The electrode with PBT-Al and PCT-Al current collector shows less polarization at 10 C than the other two. The EIS test (Fig. 6) also shows the diameter of the semi-circle in the order of PAT-Al>Al>PBT-Al>PCT-Al, and this represents the same order for the charge-transfer (including interfacial) resistance of the electrode. Another important difference in electrochemical performance is the cycle life (Fig. 7). The cycle performance is in the order PCT-Al=PBT-Al>Al>PT-Al. This follows the same trend as the descending order in resistance. From the above results, we find that the thickness of carbon layer is indeed important and should be thicker enough to enhance the conductive at Al surface, and highly related to the enhanced rate performance and cycle life.

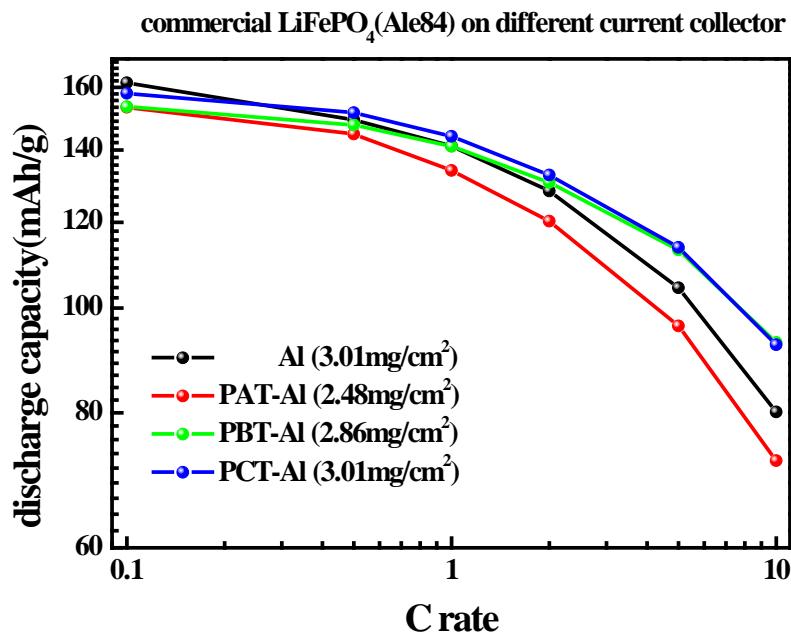


Figure 4. Rate capacities of LFPO electrodes with different current collectors.

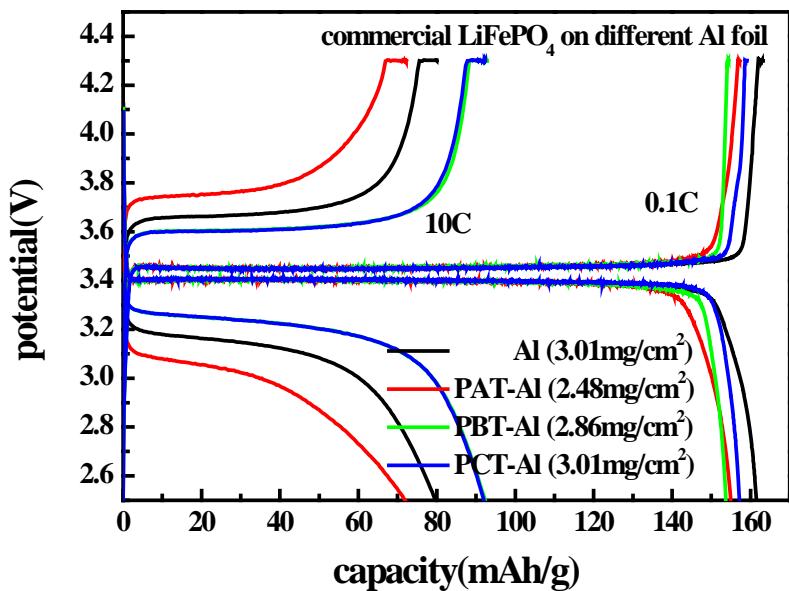


Figure 5. Charge discharge curves of LFPO electrodes with different current collectors at 0.1 C and 10 C.

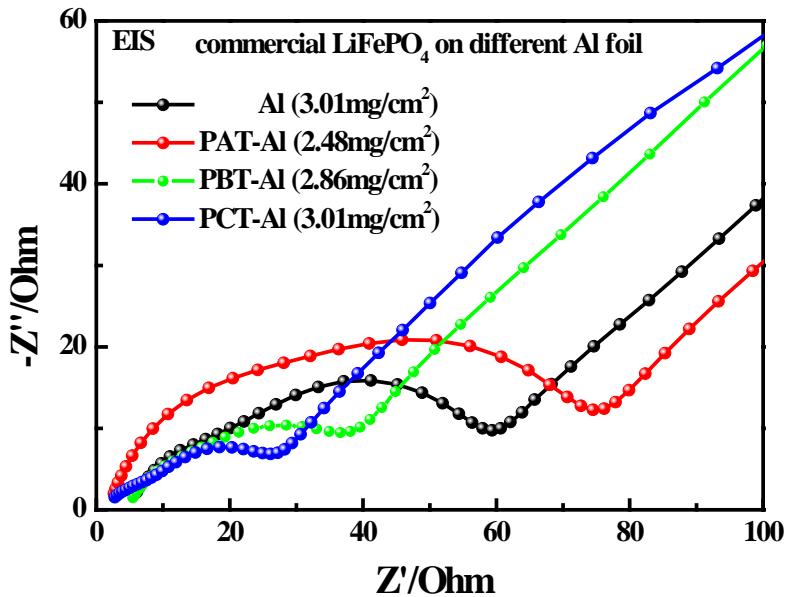


Figure 6. EIS diagrams of LFPO electrodes with different current collectors.

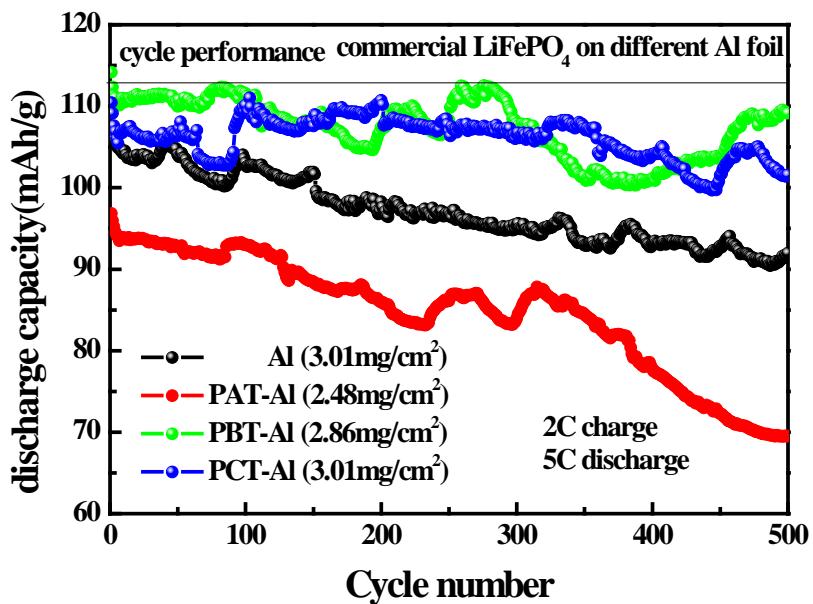


Figure 7. cycle performances of LFPO electrodes with different current collectors.

System for scale-up

The strategy for manufacturing a large area of C-coated Al foil should be separated in two part. For the first part, due to the designed plasma coating system, we can easily scale up the plasma process under high vacuum. With the same operation parameter as the one for produce PB-Al, we can increase the length of the product to more than 1.5 m as indicated in Fig. 8. The second part is to scale up the thermal treatment, which is relative more difficult because of its large space occupation and the need of extra low oxygen content in the furnace. To overcome this problem, a roll-calcination process has been created. By winding

plasma carbon coated Al foil (PB-Al) tightly on a metal roll as shown in Fig. 9a, we not only compress the occupied space dramatically, but also make the interface protect each other from the surrounding and inhibit the oxide layer formation in high temperature (Fig. 9b). The photo of sample PB-Al after roll-calcination is shown as Fig. 10. and was named as PBT-roll-Al. based on its color, the surface is not oxidized except for at within the edge area of the foil.



Figure 8. the photo of plasma carbon coated Al foil(PB-Al) with length over 1.5 m.

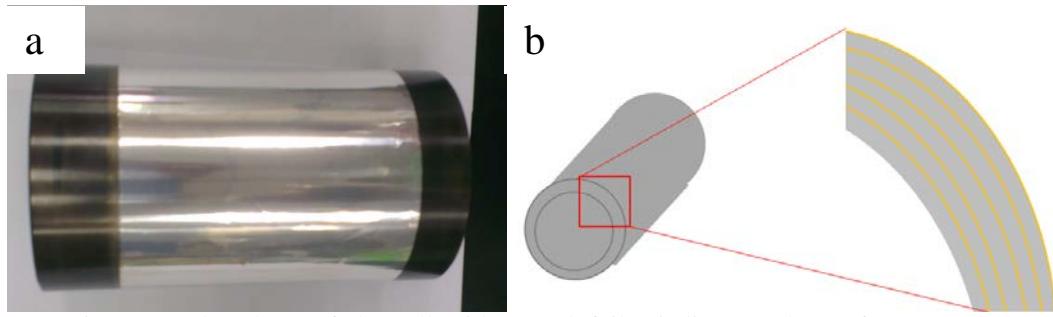


Figure 9. The photo of the roll with PB-Al foil winding on the surface(a) and the Schematic diagram of roll-calcination(b).



Figure 10. the photo of PBT-Al after roll-calcination process.

The electrochemical performance of the LFPO electrodes using current collector with scale-up surface treatment process (PBT-roll-Al) has been compared with the one from previous low-scale process (PBT-Al). The rate capacity comparison is shown in Fig. 11. It is clear that the performance of PBT-Al and PBT-roll-Al are almost the same in each C-rate. The charge/discharge voltage curves (Fig. 12) also show similar profiles at 0.1 C and 10 C. The EIS test (Fig. 13) shows the diameter of the semi-circle of the electrode with PBT-roll-Al as current collector is even slightly smaller than the one with PBT-Al. It means the surface of Al foil might be less oxidized in this scale-up process. The cycle performance is also compared in Fig. 14. The cycle life of the PBT-Al and PBT-roll-Al are also similar. It is clear that PBT-Al and PBT-roll-Al has almost the same profile in each test, and both shows better performance than the untreated Al foil.

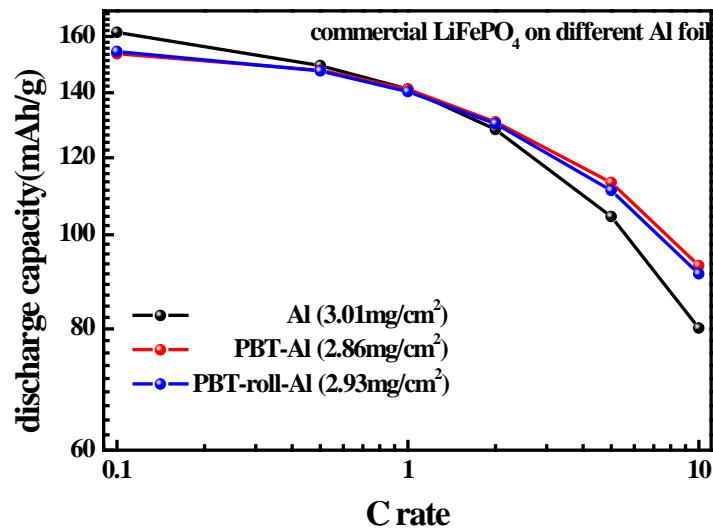


Figure 11. Rate capacity of LFPO electrodes with different current collectors.

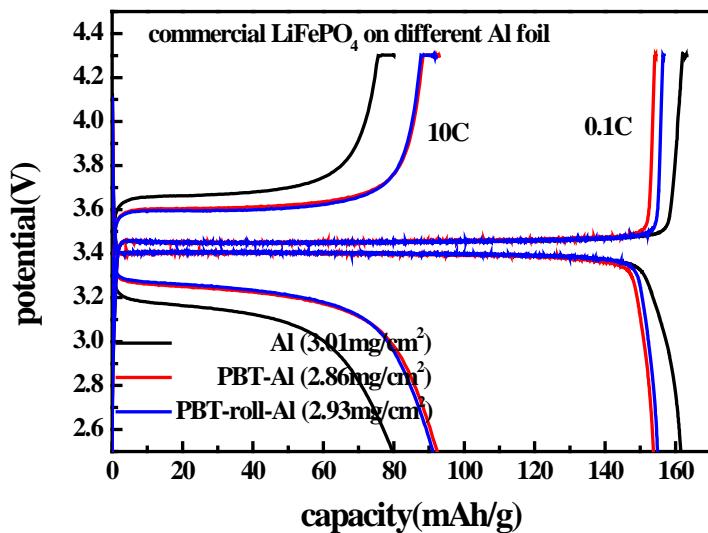


Figure 12. Charge discharge curves of LFPO electrodes with different current collectors at 0.1 C and 10 C.

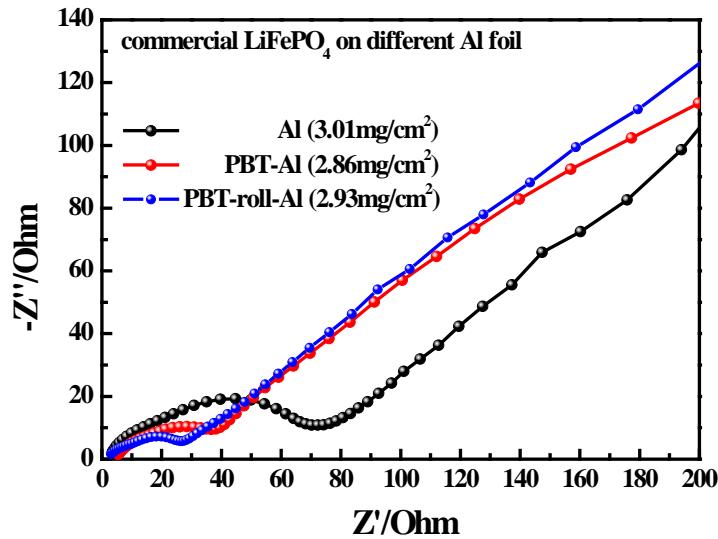


Figure 13. EIS diagrams of LFPO electrodes with different current collectors.

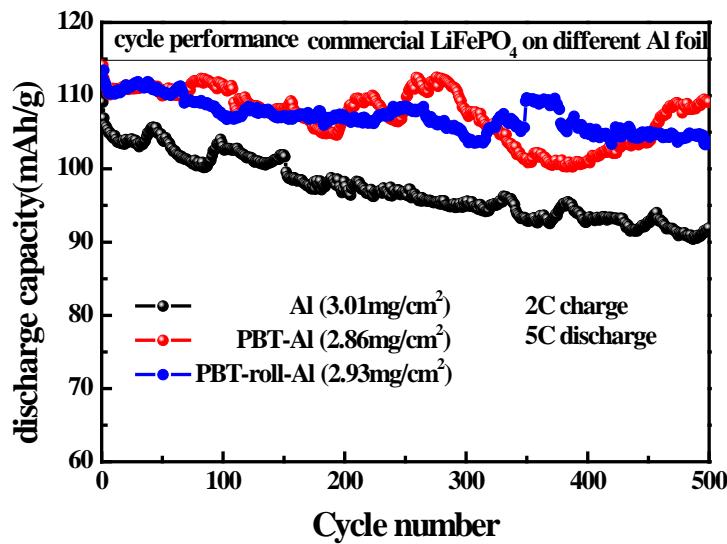


Figure 14. Cycle performance of LFPO electrodes with different current collectors.

Conclusion

The presence of insulating oxide layers at the pristine Al current collectors would impose significant resistance to current flow across the interface. Surface modification by plasma process is setup along with suitable thermal treatment. Based on the results of XPS, Raman, contact angle and CAFM, the schematic diagram of the C-coated Al is suggested as Fig. 15. There is some high conductive regions penetrating through the native alumina oxide layer, and a high conductive carbon coating on the surface makes the surface hydrophobic. When use it as current collector, hydrophobic surface can increase the contact of the surface of active material and current collector, and the electron transfer can simultaneously be enhanced. This low resistance successfully result in better rate capacity, low polarization and better cycle life.

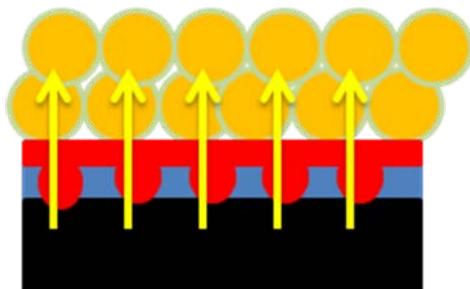


Figure 15. Schematic diagram of the modified Al foil(PT-Al) as current collector.

The relation of thickness of carbon coating and performance is studied. With the same treatment but different carbon amount, the one with thin carbon layer gets even poor performance of the electrode. However, once increasing the thickness of carbon to get a visible color change, high conductive channel will be formed on the surface and give obvious positive effect on the performance of the electrode. The scale up of this surface modification process is also proved to be feasible by overcoming the oxidation problem after high temperature treatment. The roll-calcination technique indeed works for isolating the Al surface from the oxygen, and helps to scale up the manufacture of the product with same preforming as one in low scale.